

Momentum densities and Compton profiles of alkali-metal atoms

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Abstract. It is assumed that the dynamics of valence electrons of alkali-metal atoms can be well accounted for by a quantum-defect theoretic model while the core electrons may be supposed to move in a self-consistent field. This model is used to study the momentum properties of atoms from ³Li to ³⁷Rb. The numerical results obtained for the momentum density, moments of momentum density and Compton profile are found to be in good agreement with the results of more detailed configuration-interaction calculations for the atom ³Li. Similar results for ¹¹Na, ¹⁹K and ³⁷Rb are compared with the corresponding Hartree–Fock–Roothaan values only, for want of data from other realistic calculations.

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1. Introduction

The alkali-metal atoms are made up of closed shells with one valence electron which can be excited very easily leaving the other electrons in a much more tightly bound core. The excited electron may be regarded to move in a potential due to the nucleus and to the core electrons, and spend much of its time in an outer region where the nucleus is screened by the core electrons and where the potential is of Coulomb form, and some fraction of its time penetrating the region of the core. The stronger attractive potential of the core region causes the orbit to precess. As opposed to this, there is no precession of the closed elliptical orbit in a pure Coulomb potential [1]. The precession of the orbit originating from core penetration of the valence electron modifies the hydrogenic expression for the energy eigenvalues. For brevity, we call these electrons as non-hydrogenic. For non-hydrogenic electrons the principal quantum number n is replaced by an effective quantum number ν and the quantum defect μ is defined by

$$\mu = n - \nu. \quad (1)$$

It is well known that the quantum defect μ is constant in a particular series (constant n and varying l) and is obtained traditionally by fitting the experimental binding energy

although there are isolated attempts to compute the values of μ without resorting to experimental data [2]. The concept of half empirical quantum-defect method was introduced in the early works of quantum mechanics and played a significant role in spectroscopic studies. Seaton *et al* [3] carried out elaborate studies on the quantum-defect method and gave it a more mature status, currently known as the quantum-defect theory (QDT). A significant feature of the QDT is that the value of the quantum defect determines not only the energy of the states but also the spatial character of the wave function. For the general non-hydrogenic case Seaton provided an asymptotic form of the wave function given by [4].

$$P_{vl}(r) = [\chi(v)v^2\Gamma(v+l+1)\Gamma(v-l)]^{-1/2}W_{v,l+1/2}\left(\frac{2r}{v}\right), \quad (2)$$

where $W_{v,l+1/2}(\cdot)$ stands for the irregular Whittaker function and

$$\chi(v) = 1 - \frac{2}{v^3} \frac{d\mu(\varepsilon)}{d\varepsilon}. \quad (3)$$

Equation (2) is written in Hartree atomic units. We shall follow this convention throughout. For alkali-metal atoms $\mu(\varepsilon)$ is a slowly varying function of the bound-state energy ε such that $\chi(v) = 1$. As opposed to eq. (2) the hydrogenic wave function is given in terms of the regular Whittaker function. It is of interest to note that the wave function in eq. (2) has been found useful over the entire configuration space. For calculational simplicity one often works with even a truncated asymptotic expansion for the function $W_{v,l+1/2}(\cdot)$ [5]. In any case we shall work with the full form. The quantum-defect theoretic wave function is believed to take better account of exchange and correlation effects than it is possible in a potential model representation as in the Hartree–Fock description. This point was established by Fano [6] and by Mies [7] more or less independently of each other. Both of them derived a relationship between the quantum-defect treatment and configuration mixing. Thus we propose to make use of the non-hydrogenic wave functions in eq. (2) to study the effect of electronic correlation on momentum space properties of the alkali-metal atoms. We achieve this by calculating results for electron momentum density and Compton profiles. To make a useful check on the quality of quantum-defect-theoretic description of alkali-metal atoms, we compare our results with those obtained in a Hartree–Fock–Roothaan calculation. More significantly, we confront our values for momentum density, moments of momentum density and other related quantities with the corresponding numbers found from detailed configuration-interaction calculations [8,9].

In §2 we give an exact hypergeometric-function representation for Seaton’s non-hydrogenic wave function in momentum (p) space and show how this result could be used to calculate electron momentum density $\Pi(p)$ and its moments $\langle p^k \rangle$. The quantities $\Pi(p)$ and $\langle p^k \rangle$ have been found to be most sensitive to correlation effects. In addition to this, the values of Compton profile are also expected to be significantly affected by electronic correlation [10]. Thus we feel that the use of Seaton’s wave functions in momentum space to calculate numbers for $\Pi(p)$, $\langle p^k \rangle$ and $J(q)$ (Compton profile) and compare them with the results of other realistic calculations [8,9] is interesting. In this section we also give the formula for $J(q)$ to be used for numerical calculations. In §3 we present our calculated values for $\Pi(p)$, $\langle p^k \rangle$ and $J(q)$ for alkali-metal atoms from ${}^3\text{Li}$ – ${}^{37}\text{Rb}$ and compare them with other available results of more detailed calculations. In particular, we point out

that a one parameter quantum-defect theoretic wave function does not fare worse than a configuration-interaction wave function containing 1760 terms [11]. Obviously, the merit of the present approach is its simplicity.

2. Theoretical background

The wave function in eq. (2) is given in the configuration space. Our first task will be to express this wave function in the momentum space since the properties to be studied are determined by the momentum-space wave function. The irregular Whittaker function in eq. (2) appears as an awkward analytical constraint to express Seaton's non-hydrogenic wave function in the momentum space. In the recent past one of us [12] constructed a hypergeometric-function representation for the Fourier transform of $P_{v0}(r)$ to read

$$g_v(p) = \left(\frac{2}{\pi v}\right)^{1/2} \frac{4v}{(1+p^2v^2)^2} C_v(\zeta) \quad (4)$$

with

$$C_v(\zeta) = \frac{v \sin[v(\theta - \pi)]}{\sin(\theta - \pi)} + \frac{\sin(v\pi)}{\pi} \left[-\frac{1}{2(1-\zeta)} + \frac{z}{z^2-1} \{F(1, v; 1+v; z) - F(1, v; 1+v; 1/z)\} \right], \quad (5)$$

$$2\zeta = z + z^{-1} = \frac{pv - i}{pv + i} + \frac{pv + i}{pv - i} \quad (6)$$

and

$$\theta = \arccos \frac{p^2v^2 - 1}{p^2v^2 + 1}. \quad (7)$$

To write eq. (4) we have omitted the subscript $l = 0$ since the valence electron of all alkali-metal atoms are s electrons. The function $g_v(p)$ is real since z and $1/z$ are complex conjugate to each other and, also the Gaussian hypergeometric function $F(\cdot)$ occurring in eq. (5) are well-defined [13].

In a purely hydrogenic and/or Hartree-Fock model, the orbital contribution to the spherically averaged momentum density is given by [14]

$$\Pi_{nl}(p) = (4\pi)^{-1} |g_{nl}(p)|^2 \quad (8)$$

such that

$$\Pi(p) = \sum_{nl} \Pi_{nl}(p). \quad (9)$$

The function $g_{nl}(p)$ stands for the momentum-space wave function of the (n, l) orbit in the central field of the atomic nucleus. Here the sum extends over all occupied orbitals in the atom. In the quantum-defect theoretic model we shall use

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$$\Pi(p) = \sum \Pi_{nl}(p) + \Pi_v(p) \quad (10)$$

with

$$\Pi_v = (4\pi)^{-1} |g_v(p)|^2, \quad (11)$$

the contribution made by valence electrons. In eq. (10) the sum includes the quantum numbers of the core electrons only.

The moments of electron momentum density are defined [15] as

$$\langle p^k \rangle = 4\pi \int_0^\infty p^{k+2} \Pi(p) dp, \quad -2 \leq k \leq 4. \quad (12)$$

In the impulse approximation the isotropic Compton profile is simply related to the electron momentum density. As in the case of $\Pi(p)$ and $\langle p^k \rangle$ we shall study the Compton profile in terms of the expression written as

$$J_{\text{HF}}(q) = \frac{1}{2} \sum_{nl} \int_q^\infty |g_{nl}(p)|^2 p dp \quad (13)$$

and

$$J_{\text{QDT}}(q) = \frac{1}{2} \left[\sum_{nl} \int_q^\infty |g_{nl}(p)|^2 p dp + \int_q^\infty |g_v(p)|^2 p dp \right]. \quad (14)$$

The line profile $J(q)$, characterized by the usual Compton parameter q , represents the broadening of the Compton line due to the motion of the target electron and we have written eqs (13) and (14) in the impulse approximation. The impulse model is expected to be quite satisfactory for the present study since the valence electrons of alkali-metal atoms are loosely bound and give a major contribution to profile values.

3. Results and discussion

Using the values of the quantum defect [16] $\mu_{\text{Li}} = 0.4115$, $\mu_{\text{Na}} = 1.3729$, $\mu_{\text{K}} = 2.2295$ and $\mu_{\text{Rb}} = 3.1952$ for the ground state of the valence electron and the parameters of the Hartree–Fock–Roothaan wave function [17], we have computed the results for $\Pi(p)$, $\langle p^k \rangle$ and $J(q)$. To that end we have made use of the formulas in (8)–(14) in conjunction with quantum-defect theoretic momentum-space wave function given in (4) and a corresponding expression for the Hartree–Fock–Roothaan wave function given elsewhere [18]. In table 1 we present the results for momentum density $\Pi(p)$ as a function of p for ${}^3\text{Li}$ with a view to compare our data with the results of more elaborate configuration-interaction (CI) calculations [8,9]. In the configuration-interaction method one calculates the momentum density of the whole atom and our results $\Pi_{\text{HF}}(p)$ refer to $\Pi(p)$ given in (9). The momentum density $\Pi_{\text{QDT}} = 2\Pi_{1s,\text{HF}}(p) + \Pi_{3s,\text{QDT}}(p)$. To facilitate comparison with the CI data we have given in braces the results from Esquivel *et al* [8] and Sarsa *et al* [9]. From the data in the table it is clear that both $\Pi_{\text{HF}}(p)$ and $\Pi_{\text{QDT}}(p)$ are monotonically decreasing function of p and for $p \leq 0.2$ a.u., $\Pi_{\text{HF}}(p) > \Pi_{\text{QDT}}(p)$. For $p > 0.2$ a.u., $\Pi_{\text{HF}}(p) \approx \Pi_{\text{QDT}}(p)$. Looking closely into the table we see that the values for configuration-interaction momentum

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density are in fairly good agreement with those for $\Pi_{\text{QDT}}(p)$ for small p values only. For $p \geq 0.7$ a.u., the results for $\Pi_{\text{QDT}}(p)$ fall rather rapidly towards zero when compared with the CI results. However, one can attempt to improve on the large p behaviour of $\Pi_{\text{QDT}}(p)$ by working with QDT wave functions which exhibit improved behaviour [19] as $r \rightarrow 0$. In table 2 we present similar results for ^{11}Na , ^{19}K and ^{37}Rb for valence electrons only. For all these atoms $\Pi_{\text{QDT}}(p) < \Pi_{\text{HF}}(p)$ for $p \leq 0.2$ a.u. and also for $p \geq 0.7$ a.u. The densities $\Pi_{\text{QDT}}(p)$ and $\pi_{\text{HF}}(p)$ exhibit the opposite behaviour in the intermediate p values. There is no CI data for comparison.

In table 3 we display the results for $\Pi(0)$ and $\langle p^k \rangle$ for ^3Li . We have shown the sub-shell contributions separately. The present numbers show that for $k \leq 0$, major contribution to

Table 1. Values of the momentum densities $\Pi(p)$ for ^3Li using Hartree–Fock–Roothaan and quantum-defect-theoretic wave functions.

p (a.u.)	$\Pi_{\text{HF}}(p)$	$\Pi_{\text{QDT}}(p)$
0.0	8.46741	8.36139 (8.34612)
0.1	7.25868	7.18732 (7.19456)
0.2	4.65653	4.64116 (4.68700)
0.3	2.33425	2.34672 (2.41624)
0.4	0.95913	0.97445 (1.05313)
0.5	0.33446	0.34408 (0.42426)
0.6	0.09950	0.10389 (0.18136)
0.7	0.02397	0.02552 (0.09797)
0.8	0.00377	0.00415 (0.07058)
0.9	0.00009	0.00012 (0.06026)
1.0	0.00034	0.00032 (0.05428)

Table 2. As in table 1 but for the atoms ^{11}Na , ^{19}K and ^{37}Rb .

p (a.u.)	Na		K		Rb	
	$\Pi_{\text{HF}}(p)$	$\Pi_{\text{QDT}}(p)$	$\Pi_{\text{HF}}(p)$	$\Pi_{\text{QDT}}(p)$	$\Pi_{\text{HF}}(p)$	$\Pi_{\text{QDT}}(p)$
0.0	10.2286	9.1702	17.3089	14.0419	20.6468	15.4684
0.1	8.6275	7.7909	13.6890	11.3503	15.8853	12.3354
0.2	5.2642	4.8648	6.9101	6.1385	7.3545	6.4140
0.3	2.4235	2.3343	2.3128	2.3426	2.1089	2.2951
0.4	0.8827	0.9038	0.5116	0.6559	0.3587	0.5824
0.5	0.2612	0.2910	0.0612	0.1291	0.0209	0.0957
0.6	0.0607	0.0769	0.003	0.0125	0.0034	0.0049
0.7	0.0090	0.0149	0.0061	0.0001	0.0171	0.0017
0.8	0.0002	0.0012	0.0120	0.0043	0.0208	0.0074
0.9	0.0008	0.0001	0.0124	0.0071	0.0176	0.0096
1.0	0.0022	0.0011	0.0104	0.0074	0.0128	0.0091

Table 3. Values of $\Pi(0)$ and $\langle p^k \rangle$ for ^3Li .

Model	$\Pi(0)$	$\langle p^{-2} \rangle$	$\langle p^{-1} \rangle$	$\langle p \rangle$	$\langle p^2 \rangle$	$\langle p^3 \rangle$
QDT ($2s$)	8.26146	24.7539	3.87886	0.371076	0.246238	0.383535
HF ($1s^2$)	0.099927	1.52835	1.31425	4.49213	14.448	69.7537
Total	8.361387	26.28225	5.19311	4.863206	14.694238	70.137235
CI values	8.34612	26.134	5.15190	4.91960	14.95500	71.64300

Table 4. Values of Compton profiles $J(q)$ for ${}^3\text{Li}$. The quantities $J_1(q)$, $J_2(q)$ and $J_3(q)$ stand for profile values computed using QDT, EB and HF wave functions and $\Delta J_{21} = J_2(q) - J_1(q)$, $\Delta J_{31} = J_3(q) - J_1(q)$.

q (a.u.)	J_1	J_2	J_3	ΔJ_{21}	ΔJ_{31}
0.0	2.54578	2.57596	2.59297	0.03018	0.047189
0.1	2.30585	2.33236	2.34337	0.02651	0.03753
0.2	1.76451	1.78200	1.78285	0.01749	0.01834
0.3	1.23827	1.24639	1.24204	0.00812	0.00377
0.4	0.886618	0.88864	0.884085	0.002022	-0.00253
0.5	0.696841	0.69594	0.69304	-0.000901	-0.00380
0.6	0.601699	0.59961	0.598272	-0.002089	-0.00343
0.7	0.548678	0.54609	0.545727	-0.002588	-0.00295
0.8	0.510481	0.50767	0.50777	-0.002811	-0.00271
0.9	0.476058	0.47314	0.473413	-0.002918	-0.00264
1.0	0.442024	0.43907	0.439373	-0.002954	-0.00265

Table 5. Same as in table 4, but for ${}^{11}\text{Na}$, ${}^{19}\text{K}$ and ${}^{37}\text{Rb}$.

q (a.u.)	ΔJ_{31} [Na]	ΔJ_{31} [K]	ΔJ_{31} [Rb]
0.0	0.1008950	0.1986920	0.2645240
0.1	0.0712562	0.1113750	0.1288100
0.2	0.0152483	-0.0241641	-0.0624282
0.3	-0.0186534	-0.0660259	-0.0943400
0.4	-0.0226818	-0.0389125	-0.0396181
0.5	-0.0142589	-0.0086545	0.0008435
0.6	-0.0063086	0.0035661	0.0113501
0.7	-0.0020746	0.0038243	0.0073091
0.8	-0.0006455	0.0002603	0.0002285
0.9	-0.0006439	-0.0032623	-0.0054395
1.0	-0.0011847	-0.0057042	-0.0088063

these quantities is made by the valence electron and the core contribution is always small. This tends to indicate that an inner subshell with a tight position density has very different and flat momentum distribution. However, it is not immediately clear why valence electron and core electrons interchange their role for $k > 0$. It is of interest to note that all results obtained by us are in good agreement with those of CI calculations [8,9].

Table 4 gives numbers for Compton profiles J_1 and J_3 as a function of q computed by using the QDT and HFS wave functions for comparison with J_2 obtained from a full configuration interaction study [8,9]. Here $J_1 = 2J_{\text{HF}}(1s) + J_{\text{QDT}}(2s)$ and $J_3 = 2J_{\text{HF}}(1s) + J_{\text{HF}}(2s)$. In this table we have also included the numbers for $\Delta J_{21} = J_2(q) - J_1(q)$ and $\Delta J_{31} = J_3(q) - J_1(q)$. Both ΔJ_{21} and ΔJ_{31} decrease with q and become negative for large q values. This typical behaviour is also exhibited by the values of ΔJ_{31} presented in table 5 for ${}^{11}\text{Na}$, ${}^{19}\text{K}$ and ${}^{37}\text{Rb}$. However, the change of sign of ΔJ_{31} tends to occur at relatively low q values for high Z atoms. This is shown more explicitly in figure 1 in which $\Delta J_{31}(q)$ has been plotted as a function of q . The solid curve gives the variation of $\Delta J_{31}(q)$ for ${}^{11}\text{Na}$. Similar variations for the atoms ${}^{19}\text{K}$ and ${}^{37}\text{Rb}$ are shown by the dashed curve and dashed curve with dot respectively. For example, the zeros of $\Delta J_{31}(q)$ occur at $q = 0.23$, 0.17 and 0.15 for ${}^{11}\text{Na}$, ${}^{19}\text{K}$ and ${}^{37}\text{Rb}$ respectively. These curves go through minima and then

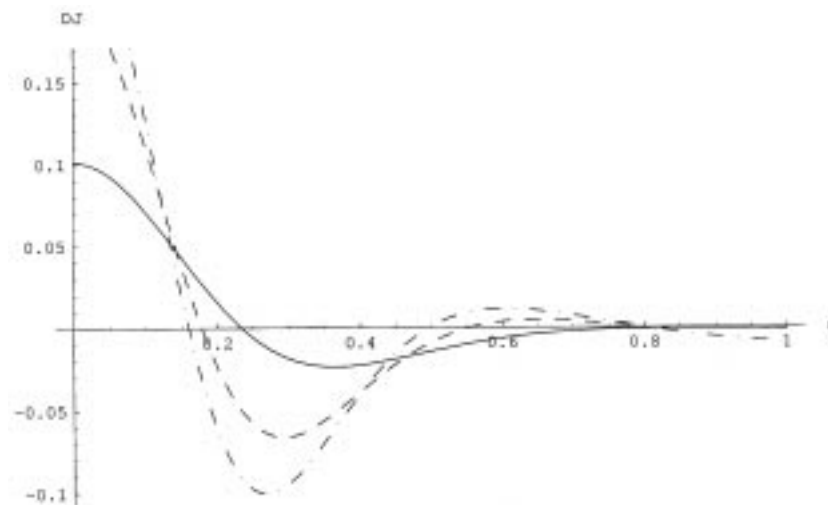


Figure 1. The difference $\Delta J_{31}(q)$ as a function of q .

Table 6. Lowering of the profile centre due to atomic correlation.

Atom	$J_{\text{QDT}}(0)$	$J_{\text{HF}}(0)$	$\Delta J(0)$	$\Delta J/n(z-1)$	$\Delta J/\sqrt{n(z-1)}$
^3Li	1.88866	1.93585	0.04719	11.797(-3)	23.595 (-3)*
^{11}Na	1.96402	2.06492	0.10090	3.363(-3)	18.422(-3)
^{19}K	2.24889	2.44758	0.19869	2.759(-3)	23.416(-3)
^{37}Rb	2.31799	2.58251	0.26452	1.470 (-3)	19.716(-3)

*The symbol $(-n)$ signifies that the entries should be multiplied by 10^{-n} .

take up positive values. We observe an opposite trend for the second zeros of $\Delta J_{31}(q)$. Here, $\Delta J_{31}(q)|_{\text{Na}} = 0$ for $q = 0.8$, $\Delta J_{31}(q)|_{\text{K}} = 0$ for $q = 0.55$ and $\Delta J_{31}(q)|_{\text{Rb}} = 0$ for $q = 0.50$. Results for ΔJ_{21} could not be displayed because $J_2(q)$ values are not available in the literature.

The lowering of profile centers with respect to Hartree–Fock ones, whatsoever, we observe in this work is entirely due to different handling of the valence electron dynamics. In table 6 we present results for $J(0)$ (QDT and HF) for the valence electrons of the alkali-metal atoms considered by us. Here we also include the values for $\Delta J(0) = J_{\text{HF}}(0) - J_{\text{QDT}}(0)$, $\Delta J(0)/n(z-1)$ and $\Delta J(0)/\sqrt{n(z-1)}$ with a view to have a quantitative estimate for the effect of electronic correlation in flattening the Compton profile. Our numbers indicate that the results for $J_{\text{HF}}(0)$ are greater than those for $J_{\text{QDT}}(0)$ for all atoms under consideration and $\Delta J(0)$ is an increasing function of Z .

As we go from lower to higher alkali-metal atoms, values of the principal quantum number n increase and at the same time we have a core produced by a larger, namely $(z-1)$ electrons. The increase in n is likely to decrease the probability of core penetration. In contrast to this, effect of the core in modifying the motion of the valence electron will

be more pronounced for higher z atoms. This simple physical realization inspired us to calculate the values for $\Delta J(0)/n(z-1)$ and $\Delta J(0)/\sqrt{n(z-1)}$. The values for $\Delta J(0)/n(z-1)$ decrease as we go along the periodic table while the results for $\Delta J(0)/\sqrt{n(z-1)}$ remain effectively constant. The latter situation reminds us of the well-known Moseley's law of X-ray spectra.

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